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HTPA Binders for Formulating High Energy, High Density Impulse, and IM Compliant Propellants

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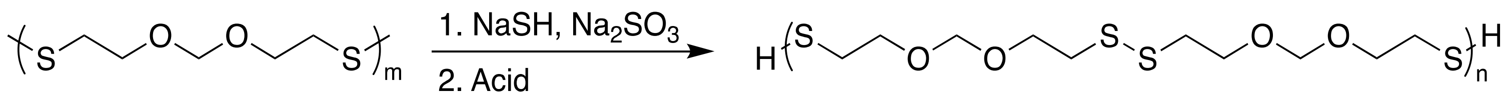
2022 CAD/PAD TEW
July 2022

Polymeric Binders in Solid Rocket Motors

Late 1800s – Nitrocellulose and double base

Early 1940s – Asphalt and oil (GALCIT/JPL/Aerojet)

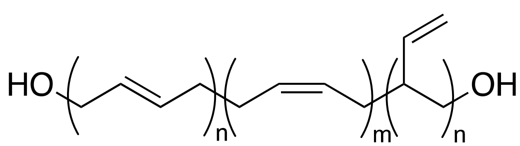
1940s – Liquid Polysulfide Prepolymers (Thiokol)



1950s – Polyvinylchloride Plastisols (ARC)

Mid 1950s – Poly(butadiene-acrylic acid) (PBAA) and Poly(butadiene-acrylonitrile-acrylic acid) (PBAN) (Thiokol)

Late 1950s – Carboxyl-terminated Polybutadiene (CTPB) (Thiokol) and Hydroxyl-terminated Polybutadiene (HTPB) (Aerojet)



Late 1950s – Hydroxyl-Terminated Polyethers, Poly(1,2-propylene oxide) (PPG) and Poly(1,4-tetramethylene oxide) (PTMEG) (Aerojet)

Late 1980s – Terathane-Polyethylene glycol (Dupont/ATK)

Slide 3

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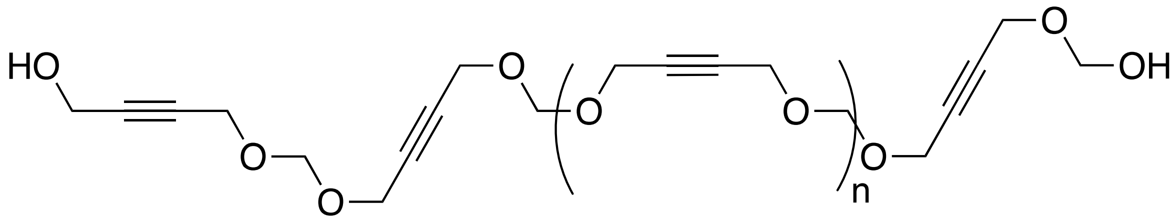
Background



- Work was done with this type of polymer in the early 1960s by Thiokol for the Bureau of Ordnance and revived by IH/NRL in 2017.
- Non-aluminized AP composite propellant using this binder type showed:
  - high I_{sp}
  - good mechanical properties
  - plateau burning rate from 700 to 2000 psi

Potential Advantages:

- Prepolymer is a linear diol, unlike a free radically-synthesized prepolymer (HTPB)
- Triple bonds and oxygen in backbone allow:
  - Lower oxidizer loadings
  - Higher energy
  - Use of nitrate esters in formulations
  - Enhanced IM performance due to lower oxidizer loading & lower cookoff temperatures

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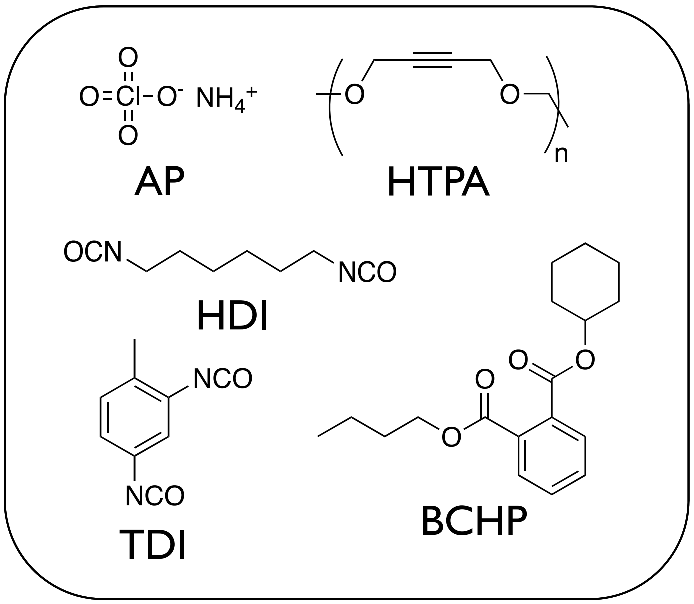
1960s Thiokol Work

Crawford bomb and small motor firings showed plateau burning behavior



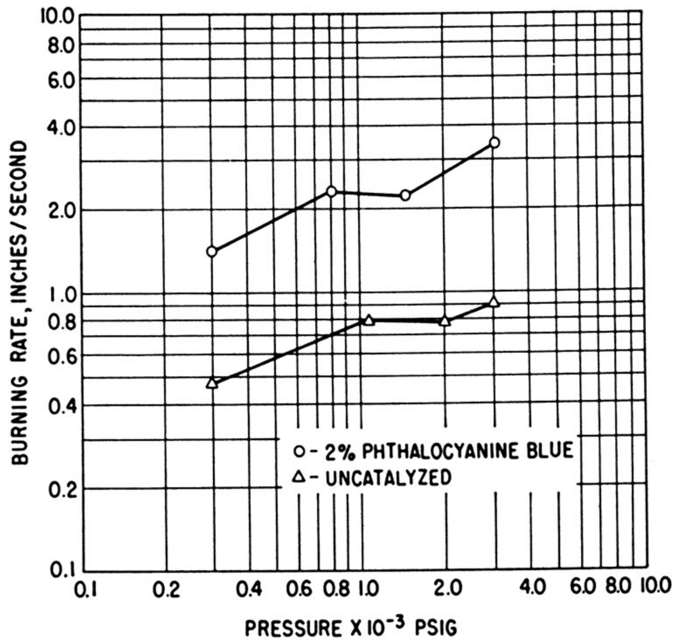


Figure 1. Burning rate of acetylenic polyurethane propellant compositions containing 80% ammonium perchlorate

From Perry et al., Adv. Propellant Chem., *54*, 118-131.

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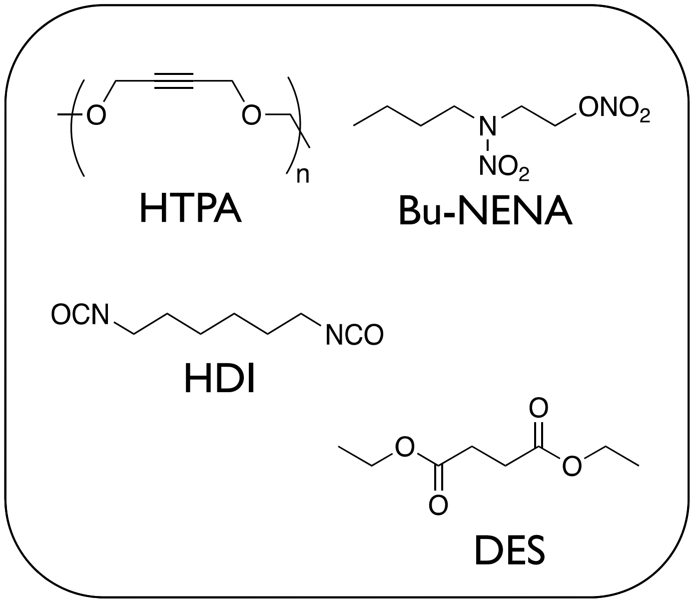
IHD/NRL Work

Synthesized HTPA was well-behaved in gumstocks



HTPA/Bu-NENA/HDI Gumstock

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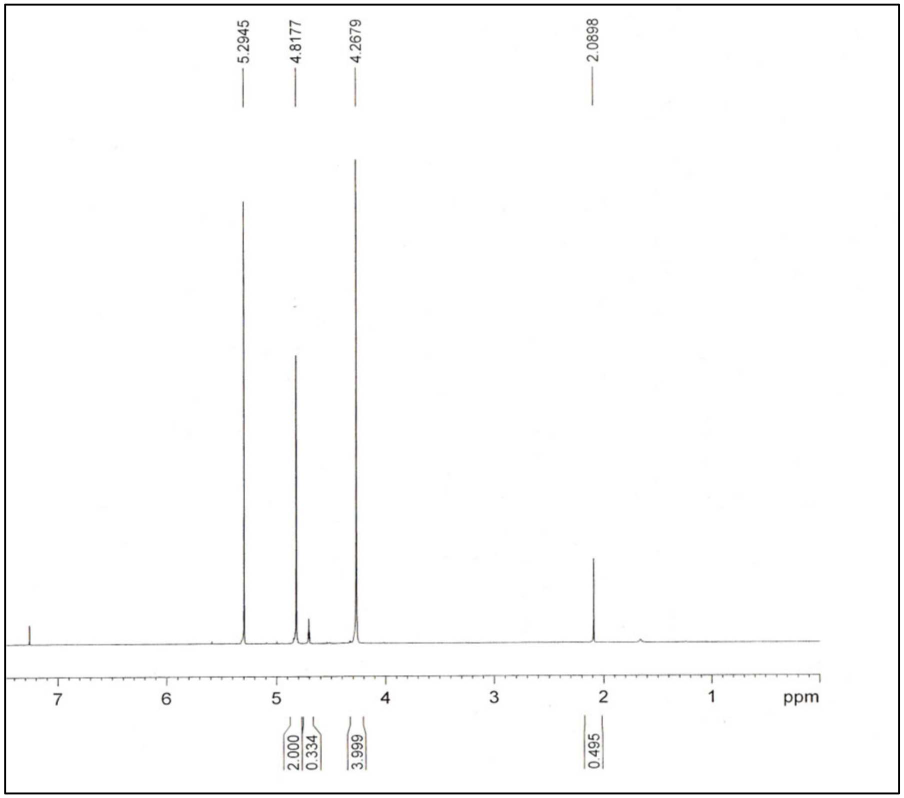
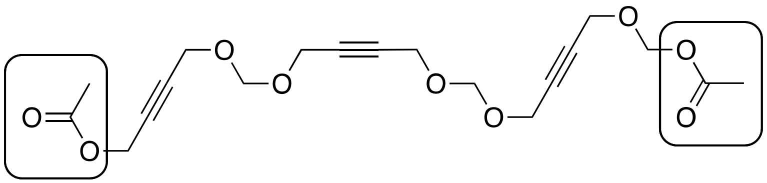
Molecular Weight



- Molecular Weight of 800-2400 g/mol determined by proton nuclear magnetic spectroscopy (NMR) on acylated HTPA
- Hydroxyl content, also determined by ^{1}H NMR was 1.1 meq/g



Acylated HTPA

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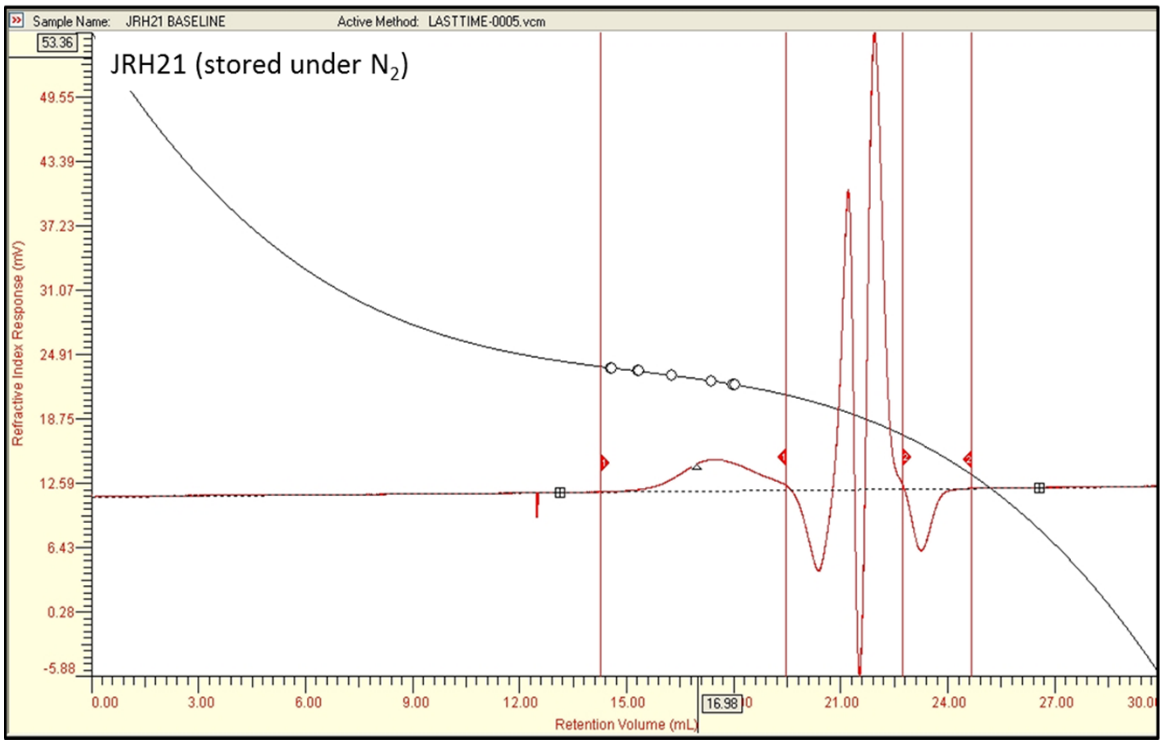
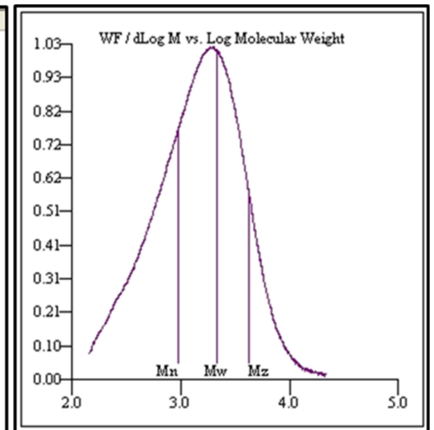
Molecular Weight





Conventional Calibration - Homopolymers : Results

Peak RV - (ml)	17.405	22.738
Mn - (Daltons)	943	0
Mw - (Daltons)	2,132	0
Mz - (Daltons)	4,170	0
Mp - (Daltons)	1,720	0
Mw / Mn	2.261	0.000
Percent Above Mw:	0.000	0.000
Percent Below Mw:	0.000	0.000
Mw 10.0% Low	278	0
Mw 10.0% High	6,855	0
RI Area - (mvml)	7.16	-3.60
UV Area - (mvml)	0.00	0.00

Gel permeation chromatography (GPC) showed comparable MWs to ^{1}H NMR

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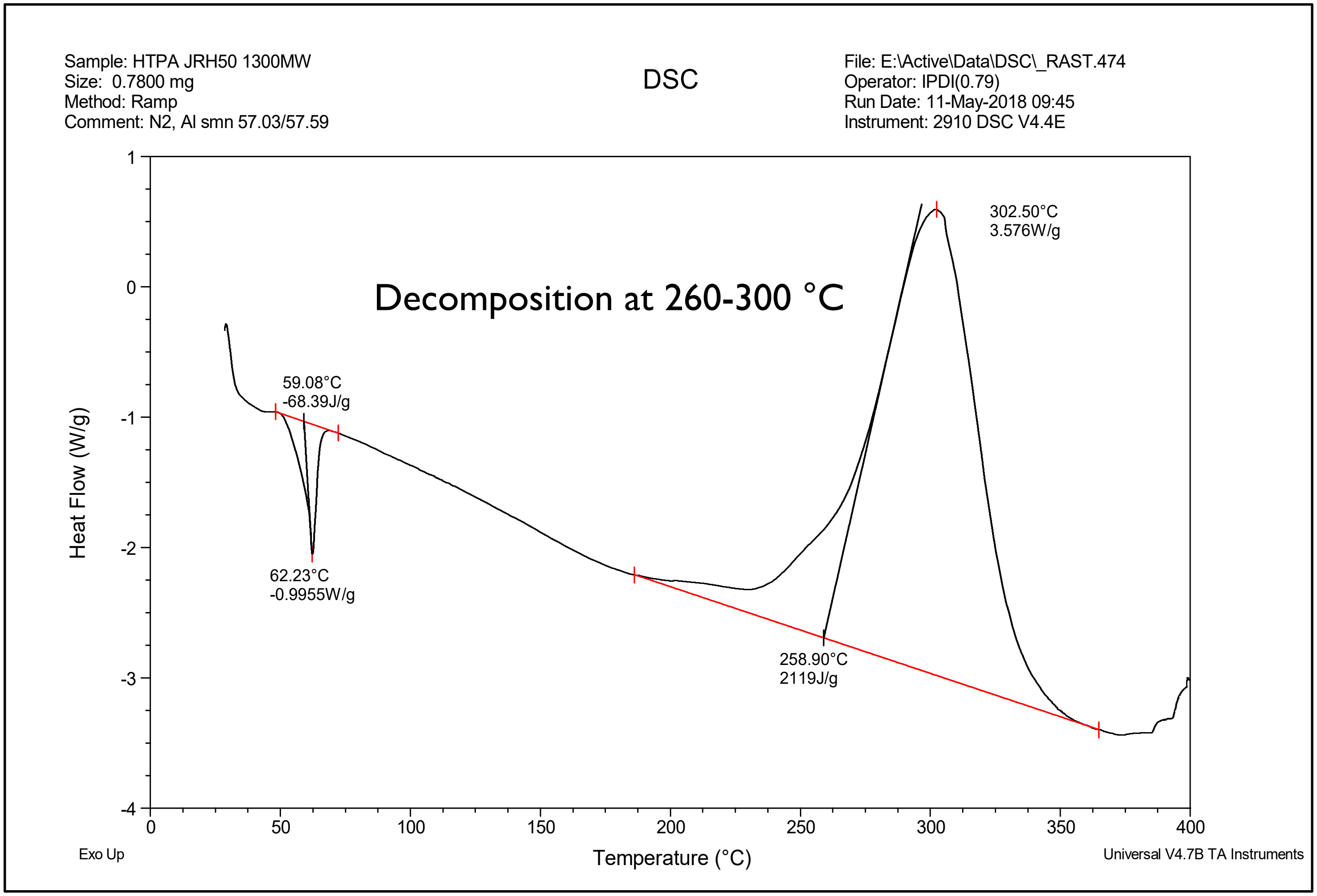
Decomposition



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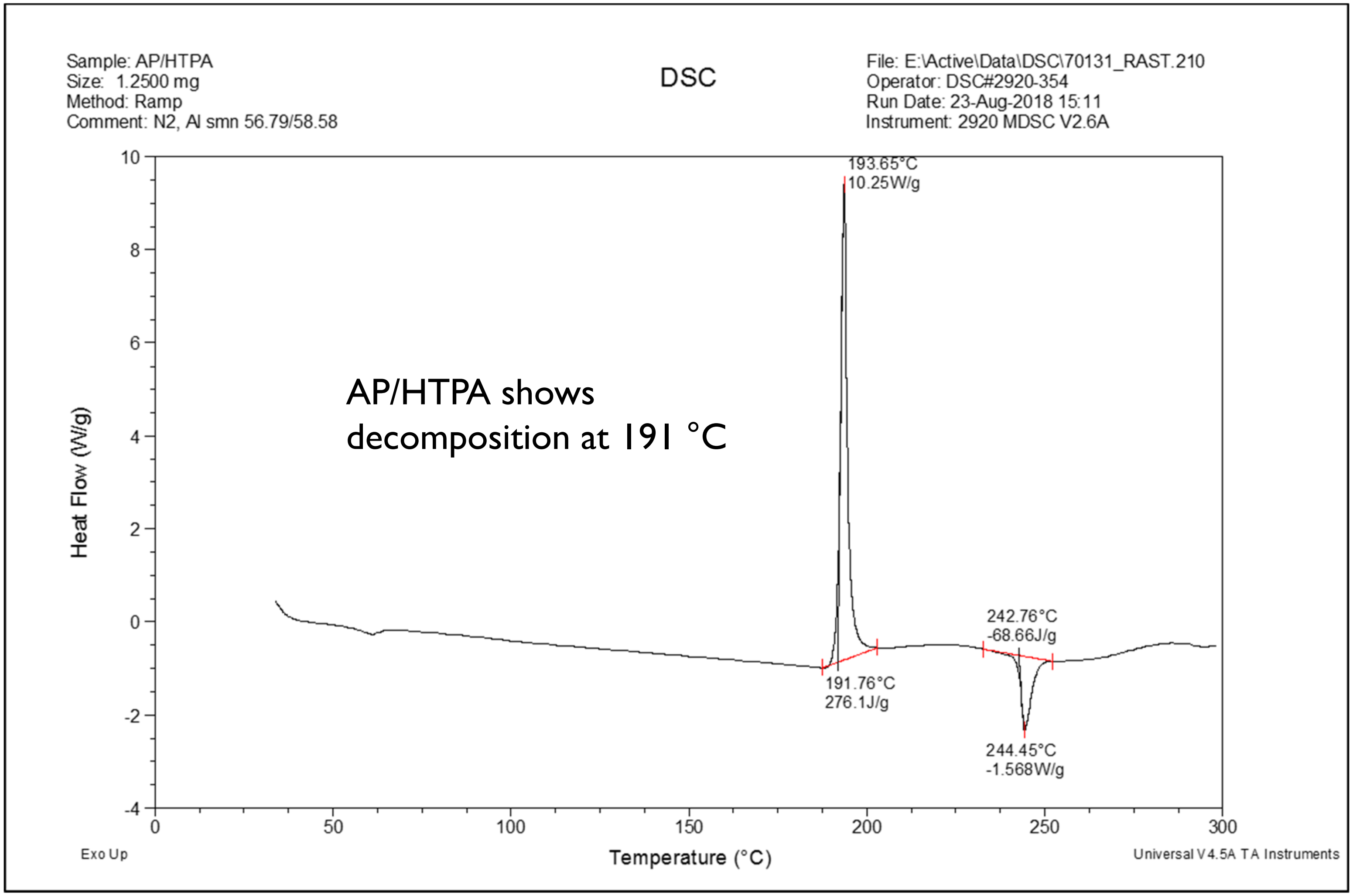
Decomposition

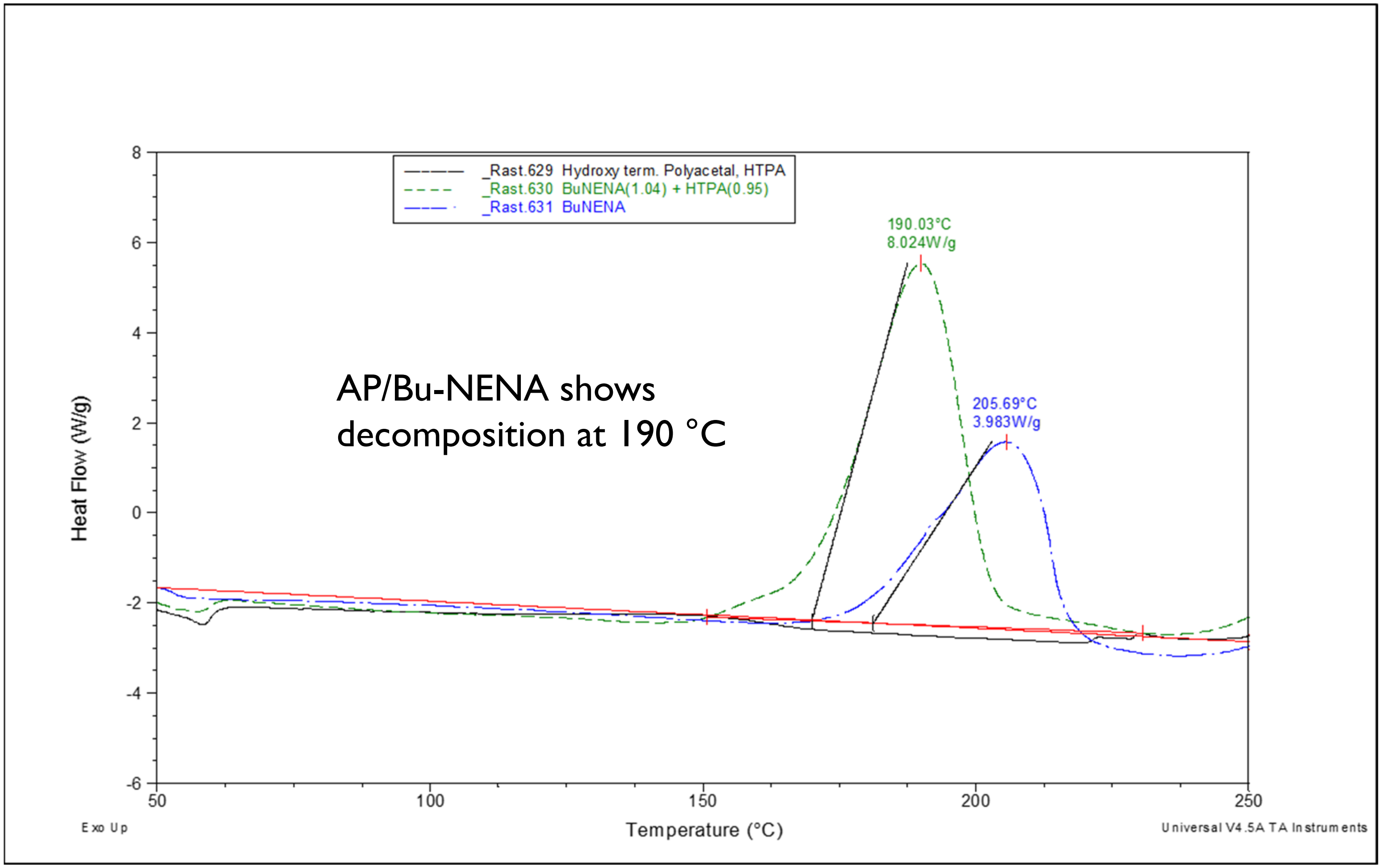


Slide 10

MB(1 Mason, Brian (CIV), 3/30/2022

MB(2 Mason, Brian (CIV), 3/30/2022

Decomposition



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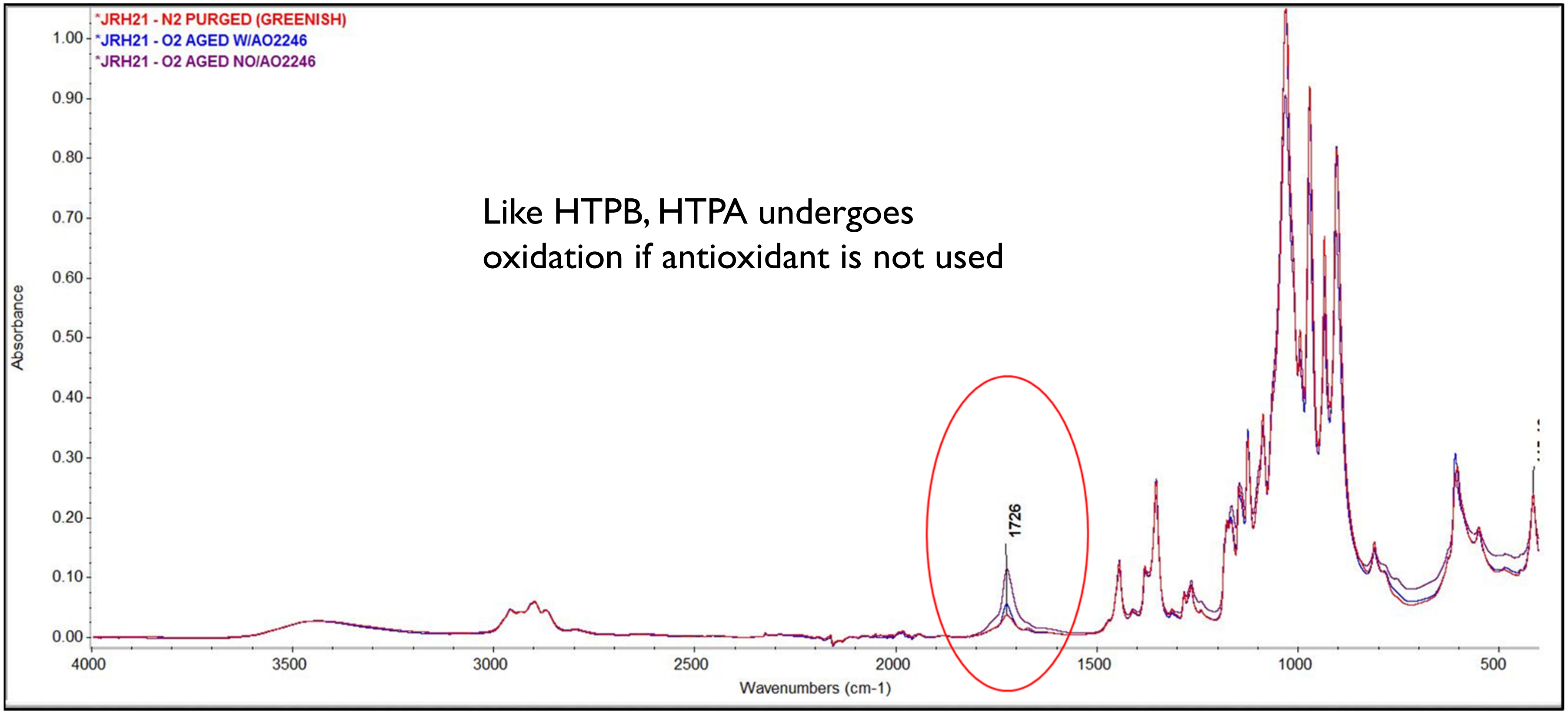
Oxidation


*JRH21 - N2 PURGED (GREENISH)
*JRH21 - O2 AGED W/AO2246
*JRH21 - O2 AGED NO/AO2246
Like HTPB, HTPA undergoes oxidation if antioxidant is not used
1726
Absorbance
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers (cm-1)

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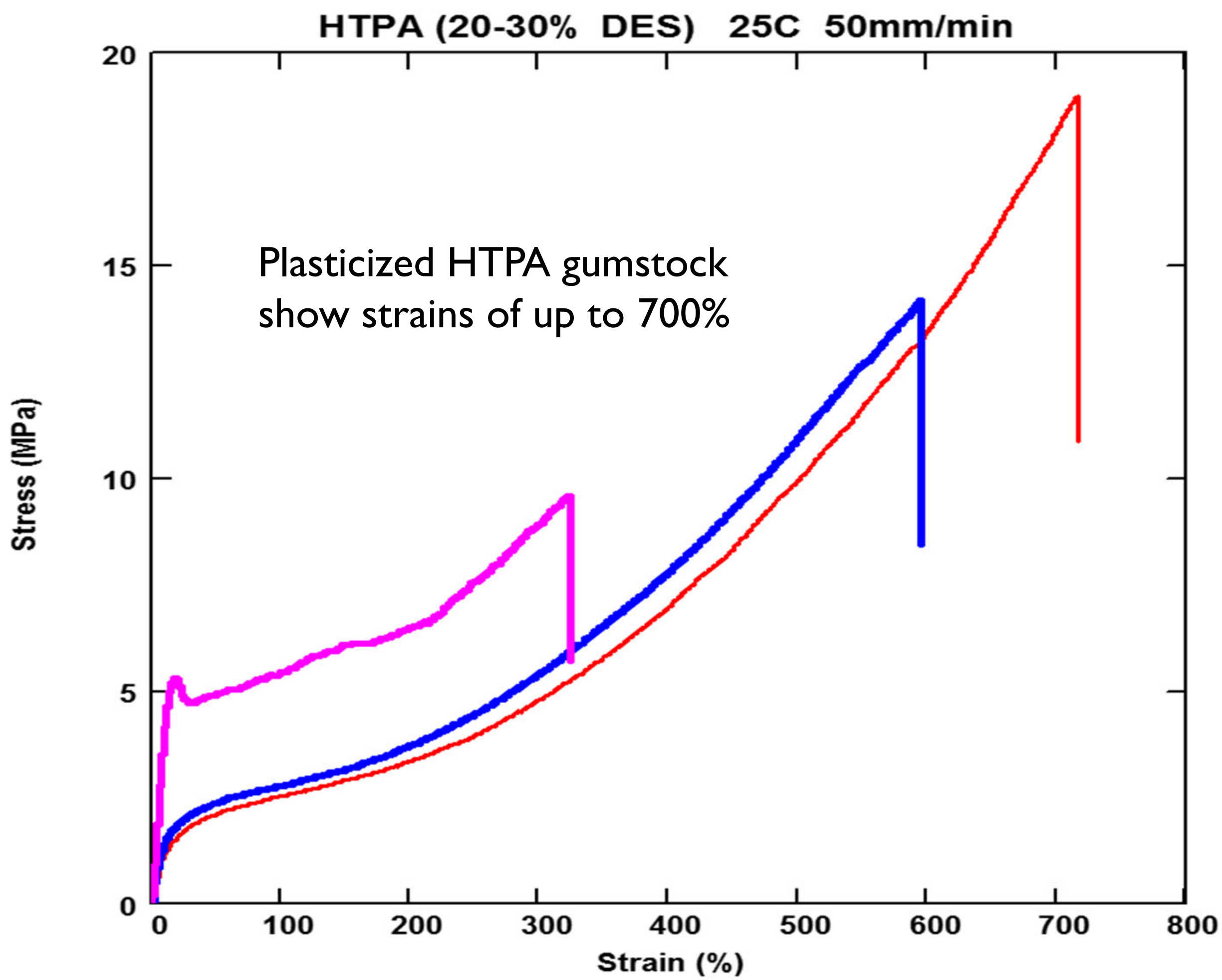
Mechanical Properties



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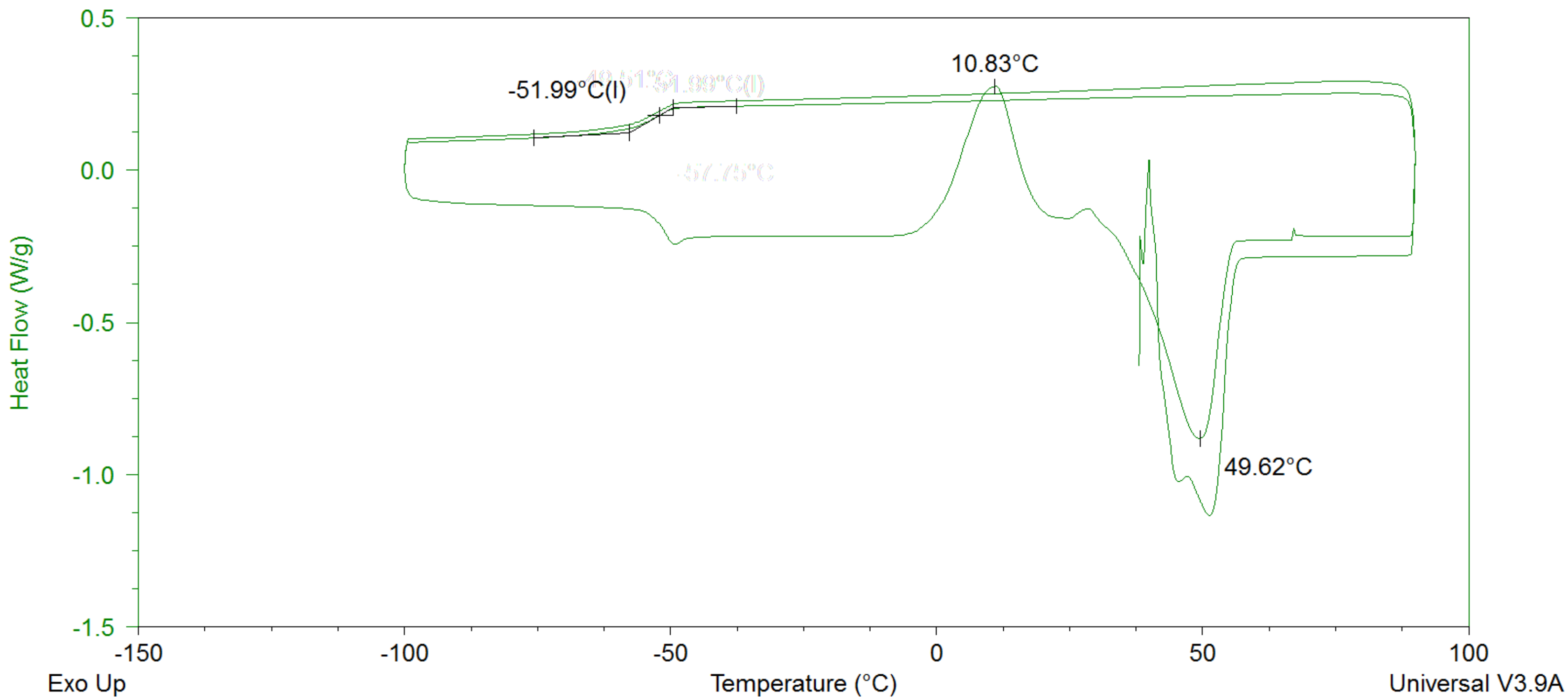
Oligomer Melting Point



Prepolymer melts at 50-60 °C, with a glass transition temperature of -52 °C

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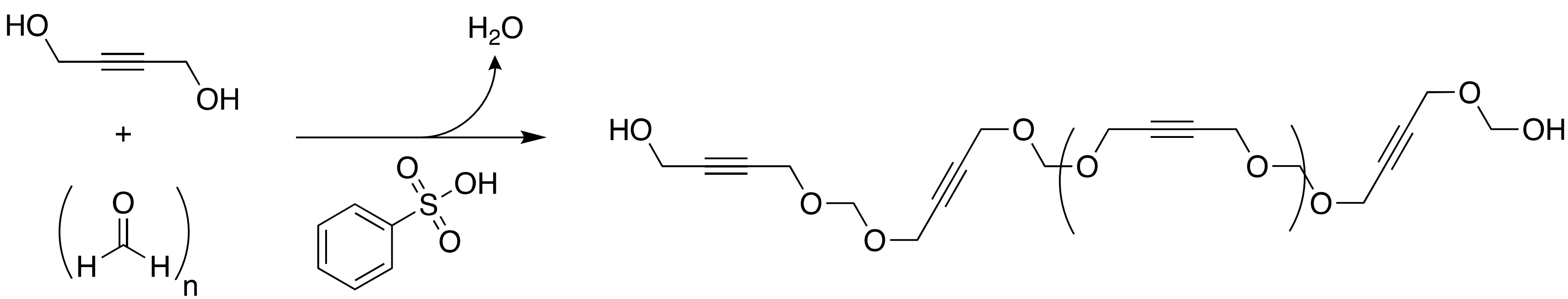
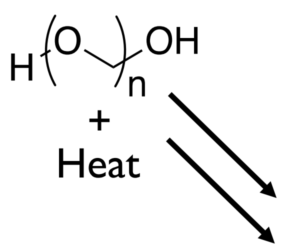
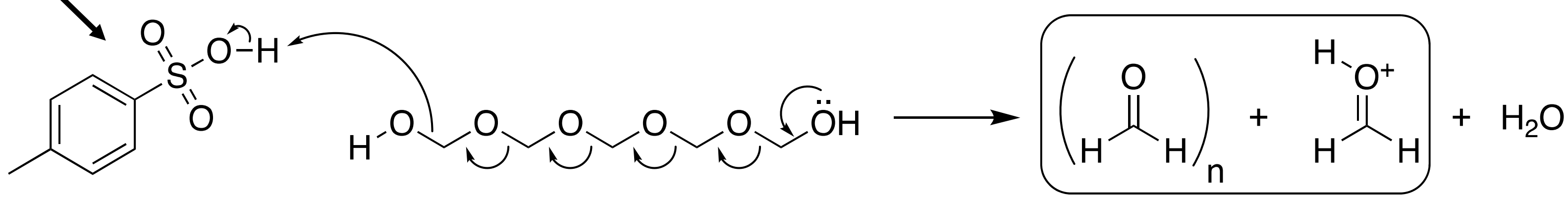
Prepolymer Synthesis



Hydroxyl-Terminated Polyacetylene (HTPA)



For convenience, formaldehyde is generated *in situ* from its polymeric form, paraformaldehyde



(Paraformaldehyde is actually much longer)

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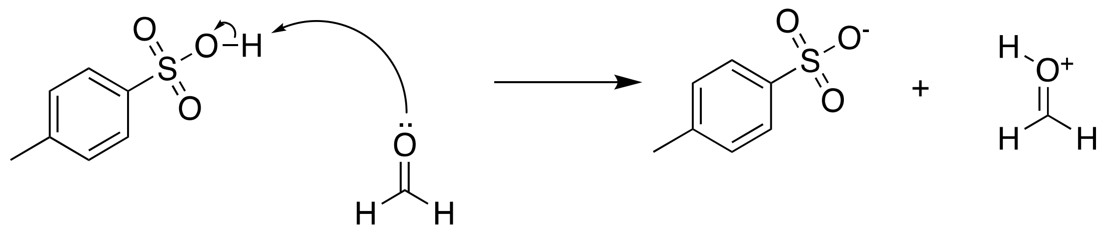
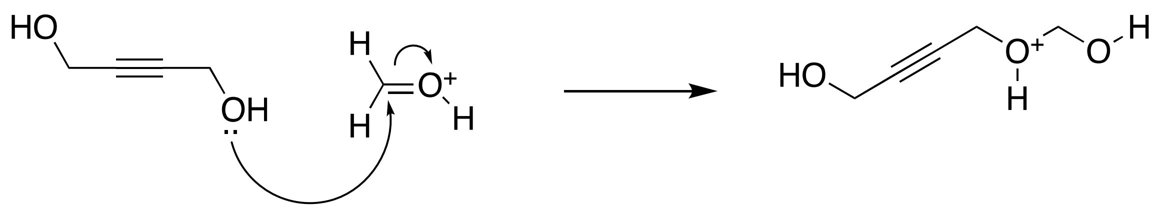
Mechanism

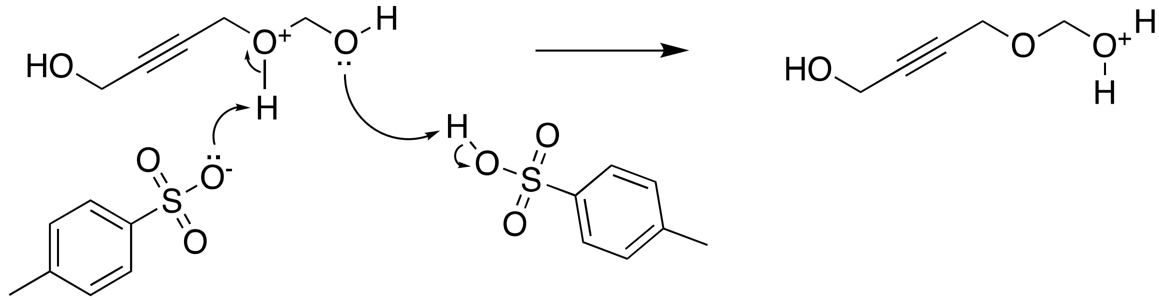
Step 1. Acid catalyst protonates formaldehyde



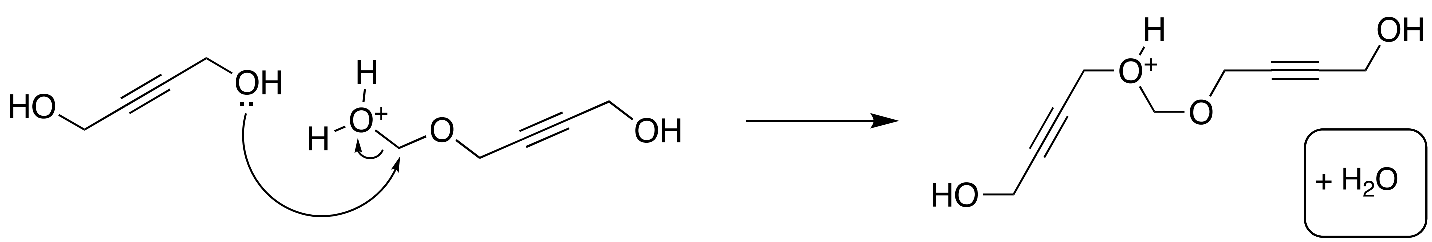
Step 2. Acetylene OH attacks protonated formaldehyde



Step 2. Catalyst protonates formaldehyde carbonyl again



Step 3. Loss of water drives the reaction forward



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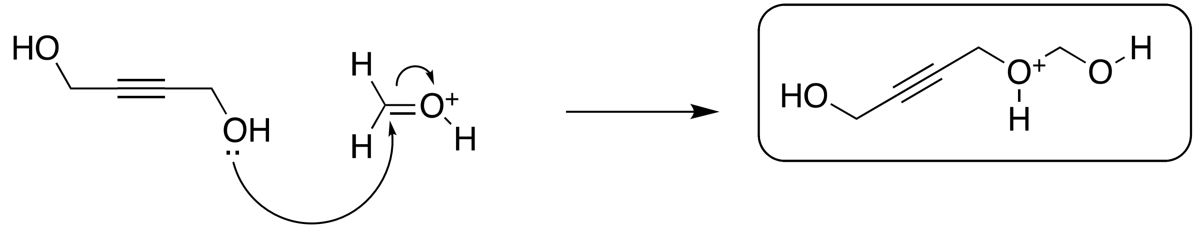
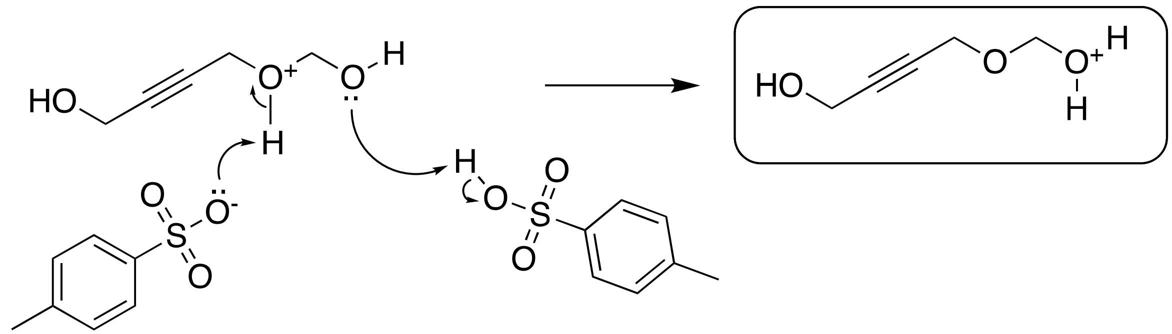
MB(2 Mason, Brian (CIV), 3/30/2022

Mechanism

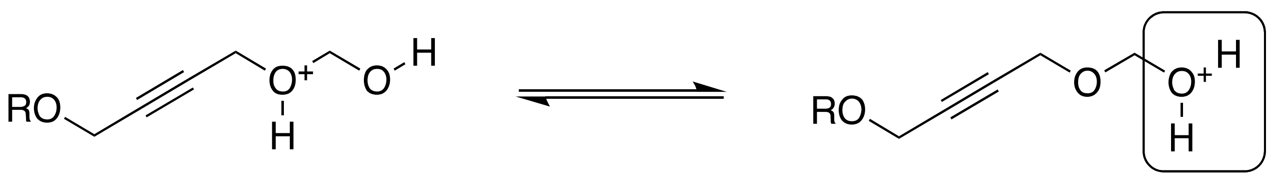
Step 2. Acetylene OH attacks protonated formaldehyde



Step 2. Catalyst protonates formaldehyde carbonyl again



Always in equilibrium...



…but loss of water drives the reaction to the right (Le Chatelier)

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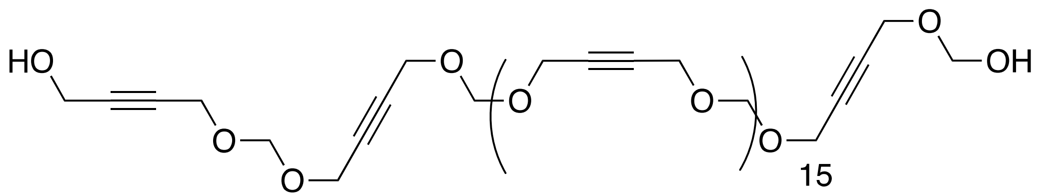
Potential Problems – Molecular Weight

What if our batches of prepolymer show too short MW?
As depicted this oligomer has a molecular weight of 2086.8 g/mol…



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MB(1	Mason, Brian (CIV), 3/30/2022
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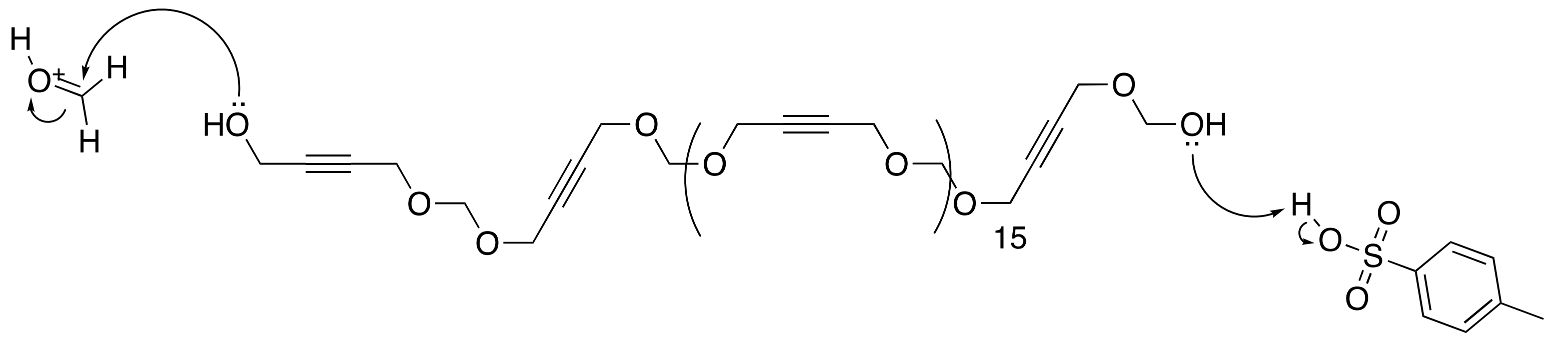
Potential Problems – Molecular Weight

What if our batches of prepolymer show too short MW?
As depicted this oligomer has a molecular weight of 2086.8 g/mol…



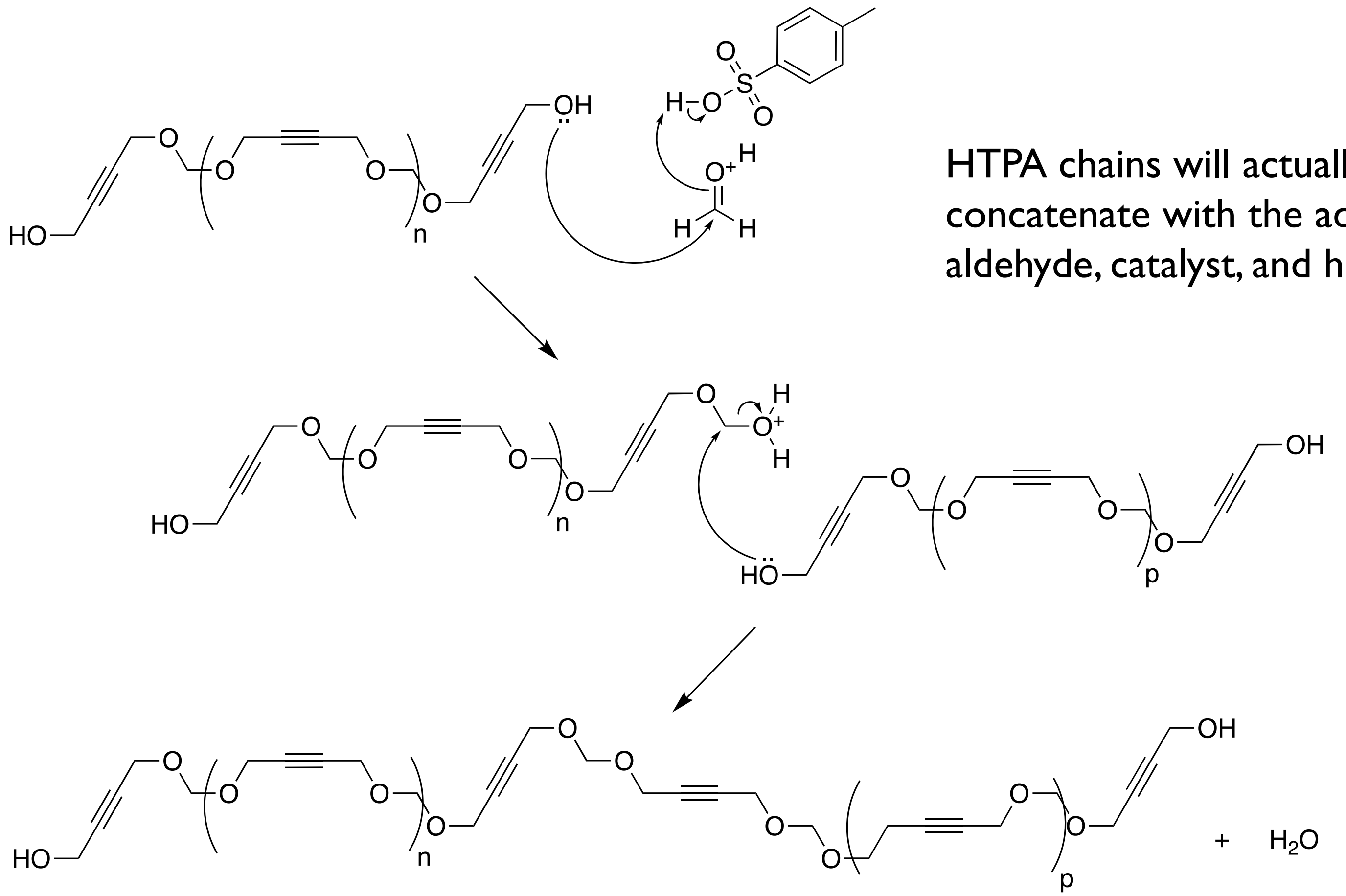
…but even after its been isolated, we can still keep reacting it to make higher molecular weight prepolymers, even years later.

Slide 19

MB(1 Mason, Brian (CIV), 3/30/2022

MB(2 Mason, Brian (CIV), 3/30/2022

Potential Problems – Molecular Weight



HTPA chains will actually concatenate with the addition of aldehyde, catalyst, and heat

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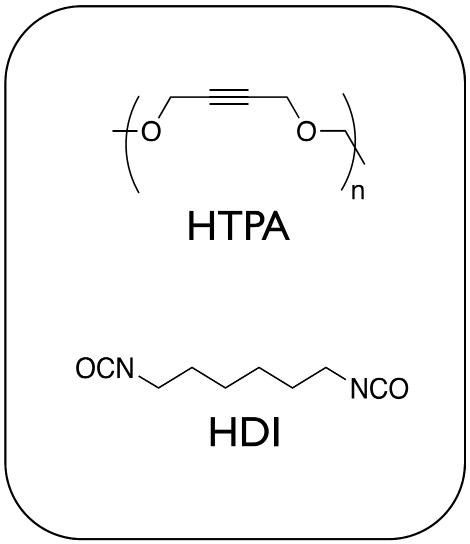
MB(2	Mason, Brian (CIV), 3/30/2022

Future Work – Lowering Glass Transition

Unplasticized HTPA formulations could be a little more amorphous



Cured Neat HTPA shows signs of crystallization

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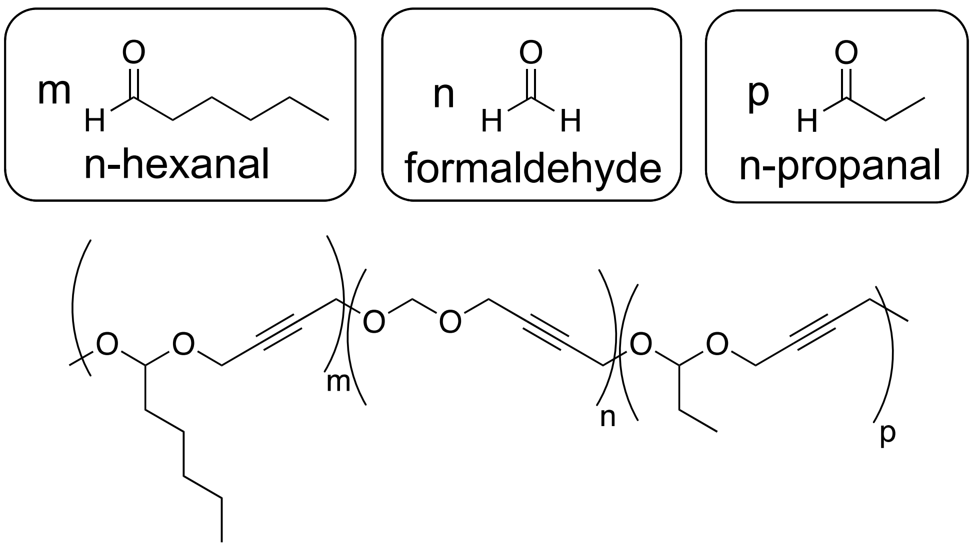
MB(2	Mason, Brian (CIV), 3/30/2022

Future Work – Lowering Glass Transition

Alternate aldehydes



Irregularity side chains break up order/crystallinity

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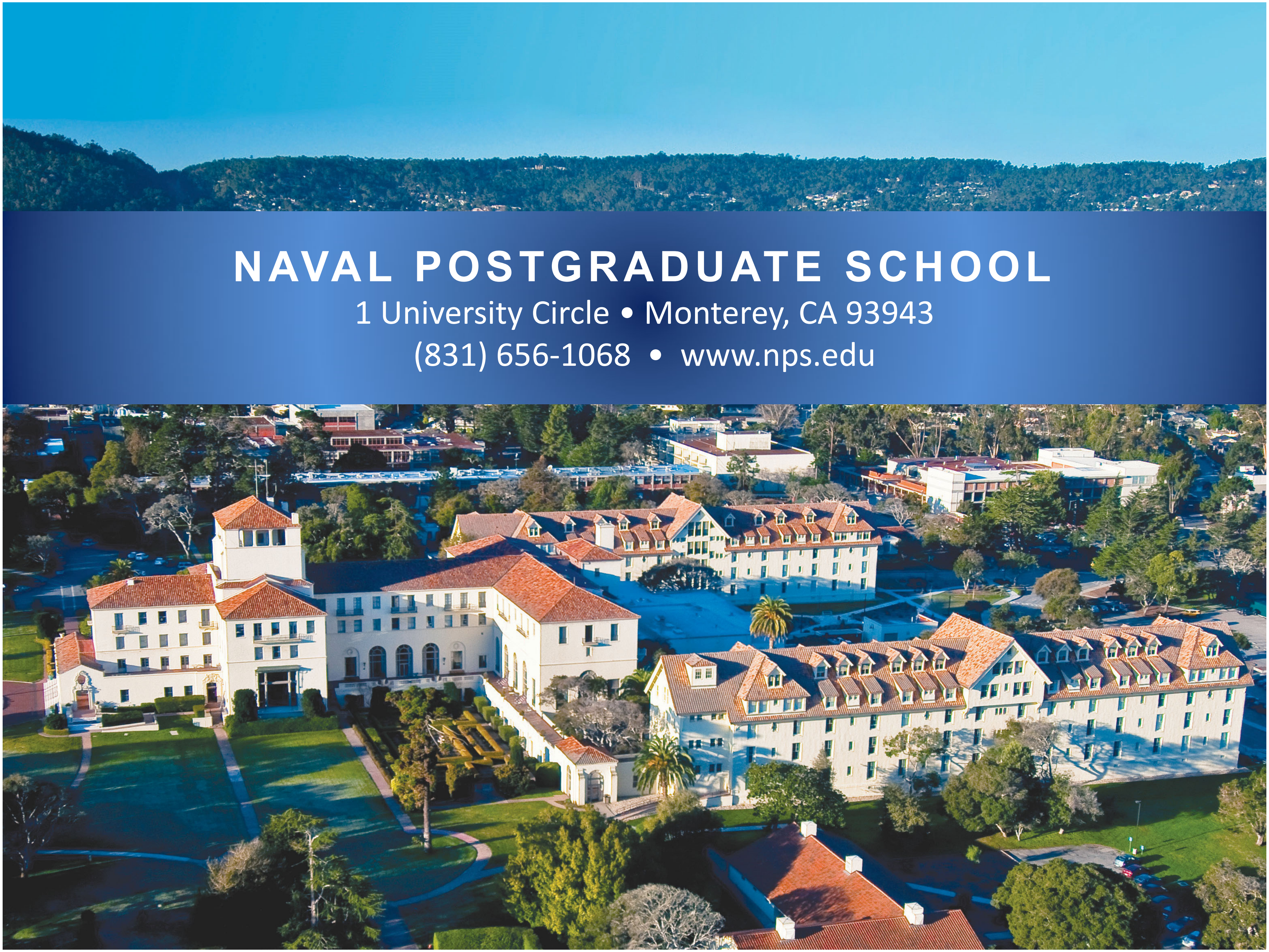
MB(2 Mason, Brian (CIV), 3/30/2022



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